### A STUDY OF EXPLOSIONS INDUCED BY CONTACT OF HYDRAZINE-TYPE FUELS WITH NITROGEN TETROXIDE

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(Prepared under Contract No. AF 33(616)-6918 by Atlantic Research Corporation, Shirley Highway at Edsall Road, Alexandria, Virginia Authors: R. Friedman, W. P. Barnes, Jr. and M. Markels, Jr.)

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#### **FOREWORD**

This report was prepared by Atlantic Research Corporation, Alexandria, Virginia, on Air Force Contract AF 33(616)-6918 under Task No. 607507 of Project No. 6075, a Study of Extinguishment and Control of Fires Involving Hydrazine-Type Fuels with Air and Nitrogen Tetroxide. The work was administered under the direction of Flight Accessories Laboratory, Aeronautical Systems Division. Mr. Benito P. Botteri and Mr. Robert E. Cretcher were project engineers for the Laboratory.

The studies presented here were conducted in the period June 1, 1961 through May 31, 1962 by the Kinetics and Combustion Division of Atlantic Research Corporation. Initiation of the project was stimulated by results reported in Technical Documentary Report ASD-TDR-61-716, also generated under the same contract. The present studies were directed by Dr. Raymond Friedman. Valuable guidance was obtained from Dr. Michael Markels, Jr. Mr. William P. Barnes, Jr., mechanical engineer, was in charge of the experimental work, and was assisted by Mr. Elmer Williams, senior technician. Professor Howard W. Emmons of Harvard University acted as consultant throughout the project, especially on fluid-dynamic aspects of experiment design and interpretation of results.

This is the final report on the contract.

#### ABSTRACT

The mechanism of explosions which may result when a hydrazine-type liquid is brought into contact with liquid nitrogen tetroxide was studied. Falling-droplet experiments showed correlation between distance of fall and probability of explosion. Sudden injection of one liquid into the other, with high-speed photography, gave nonreproducible results. Occasional explosions occurred, preceded by bubble formation. Alternate theories of the explosion phenomenon are discussed.

(21 pg 11 1.5 1 bg 1 +62)

#### PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

Branch Chief

Environmental Branch

Flight Accessories Laboratory

#### TABLE OF CONTENTS

																									1	Page
I.	SUM	MARY							•		•			•		•	•	•	•	•		•		•		1
II.	INTRODUCTION AND BACKGROUND												•		2											
	A.	Gen	eral																							2
	В.	Pro	perties of	Liqui	ds.															•				_		2
	С.		or Knowled																							
III.	exf	ERIM	ENTAL PROG	RAM .																						5
	Δ.	Gen	eral																							5
			ling-Drople																							
	ъ.	rai	TIMS-DIOPI	er Exp	GLIM	enc	в.	•	•	•	•	•	•	•	•	•	•	•	•	•	•	٠	•	•	•	)
		1.	Objective																							
		2.	Experiment	tal Pr	oced	ure																				6
		3.	Results .			•		•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•		6
	c.	Liq	uid-Li <b>qui</b> d	Inter	face	Ex	per:	Lme	ent	8			•		•	•	•									9
		1.	Objective	<b>3.</b> ,																						9
		2.	Apparatus																							
		3.	Static-In																							
		4.	Jet-Inject																							
	D.	Gas	-Liquid Exp	erime	nts	•										•										28
		1.	Objective	3.																	_					28
		2.	Apparatus																							
		3.	Results .																							
IV.	PRE	SENT	STATUS OF	KNOWL	EDGE	AN	D R	<b>EC</b> C	M	ŒN	IDE	D	FU	πu	IRE	: W	ЮR	K								29
	REF	EREN	CRS																							31

#### I. SUMMARY

Laboratory experiments have been conducted in a one-year program to study the mechanism of the occasional explosions which result when a hydrazine-type liquid is brought into contact with liquid nitrogen tetroxide with little confinement. Several hundred experiments have been performed involving falling droplets, mechanically generated liquid-liquid interfaces with and without injection of one liquid into the other, and gas-liquid contacting experiments. High-speed photography was employed. Important results are listed:

- 1. The probability of explosion when a hydrazine droplet fell into a pool of nitrogen tetroxide increased gradually with increasing distance of free fall, seven inches corresponding to 50 per cent probability.
- 2. Impact of one spring-loaded glass cell on another when a separator is removed in the presence of hydrazine and nitrogen tetroxide reproducibly gave explosion (five times in five tests).
- 3. Injection of a jet of liquid nitrogen tetroxide into liquid hydrazine through a 0.020-inch orifice under a pressure ranging from 18 to 28.5 inches Hg with no solid-solid impact led to explosion twice in eight tests. Each of the two explosions occurred about 10 milliseconds after the first appearance of a bubble, with apparently violent mixing and reaction in the interim.
- 4. When a liquid-liquid interface was formed without injection and without solid-solid impact, no explosion occurred in 16 tests with the lighter liquid in the upper cell.

The full body of results is inconsistent with the explosion being a hydrazine vapor-air explosion or monopropellant detonation. Turbulent mixing of the two liquids in the presence of vapor is believed to lead to formation of a critical concentration of an explosive substance, presumably an adduct of the two ingredients, which may be either a solute in one of the liquids (probably hydrazine) or an aerosol discrimination between these alternatives was not possible, nor was fluid-dynamic description of the critical mixing conditions for explosion. None of the geometries tested gave completely reproducible explosions, although dozens of explosions violent enough to shatter the apparatus were encountered in the course of the work.

The recommendation is made that further studies of this important problem be undertaken.

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#### II. INTRODUCTION AND BACKGROUND

#### A. GENERAL

Past experiments conducted in this program (ref. 1) have shown that sharp explosions can result when small quantities of liquid hydrazine, unsymmetrical-dimethylnydrazine, or a 50-50 mixture of these are dumped into liquid nitrogen tetroxide. The explosions did not occur reproducibly. In view of the projected widespread use of this rocket fuel system, and the potential importance of this explosion phenomenon to safe-handling practices, the present one-year program has been undertaken to gain detailed knowledge of the explosion mechanism. Objectives were to permit a logical approach to techniques for suppression of explosions arising from spills, and to provide a sound basis for extrapolation of explosive yield from small-scale tests to larger-scale incidents.

#### B. PROPERTIES OF LIQUIDS

For convenience, pertinent properties of the liquids to be considered in this program are listed:

in cure brogram are tracea.				
	Hydrazine	UDMH	50-50 Mixture	Nitrogen Tetroxide
Meiting point (°C) Boiling point (°C) Density at 25°C (gm/cc) Viscosity at 25°C (cp) Heat of vaporization (kcal/mole) Thermal conductivity (cal/cm-sec-°C) Fire point in air (°C) Allowable conc. in air (ppm) Fraction N <sub>2</sub> O <sub>4</sub> vapor dissociated to NO (one atm)	1.5 113.5 1.0 0.9 9.6 0.0012 52 0.5	-57.2 63.1 0.783 0.51 8.4 0.00049 -15 0.5	-7.3 70 0.90 0.82 0.237/gm 0.00062 1.5 0.5	-11.2 21.2 1.43 0.4 9 1 0.00030 none 2.5 0.122 at 15°C 0.185 at 25°C 0.270 at 35°C
				0.502 at 55°C

Both hydrazine and UDMH are known to be hypergolic with nitrogen tetroxide. Even when nitrogen tetroxide vapor is present in low concentration (8-15%) in air, the hydrazine-type liquids will ignite spontaneously on contact at ambient temperatures (ref. 2). It has been observed (ref. 3) that violent mixing of the two liquids, hydrazine and red fuming nitric acid, produces an explosion in three milliseconds. It has also been reported (ref. 4) that an ignition lag of 101 milliseconds is found for the case of a nitrogen tetroxide droplet falling through hydrazine vapor. In another experiment (ref. 5), a hydrazine droplet was found to ignite after "a couple of seconds", when exposed to an argon atmosphere at 75°C containing 5 per cent of nitrogen tetroxide. Past experiments in our laboratory show that hydrazine vapor as well as hydrazine liquid will ignite shortly after contact with nitrogen tetroxide vapor, but the time delay has not been measured.

#### C. PRIOR KNOWLEDGE OF EXPLOSION PHENOMENON

The term explosion cannot be precisely defined. In this report, it is used to describe an event characterized by a loud sharp report and occasional shattering of experimental apparatus when small quantities of the fuel and oxidizer are brought together. (High-speed photography at about 3000 frames per second generally has shown that the explosion occurs between frames).

The pertinent observations made during the earlier phase of the contract (ref. 1) will be reviewed.

A total of 129 tests were made in which 3 ml or less of fuel were brought into sudden contact with nitrogen tetroxide liquid by free fall. Explosions occurred in 85 cases, or in 66 per cent of the tests. Occurrence or non-occurrence of explosion was unpredictable. Neither the chemical nature of the fuel (hydrazine, unsymmetrical dimethylhydrazine, or the 50-50 mixture) nor residual moisture content of the fuel correlated with probability of explosion. In falling-droplet experiments, the droplet landing in a pool of the other liquid, there was indication of a positive correlation between height of fall and probability of explosion. A height of 17 inches was adequate to give fairly consistent explosions.

Other dumping tests were made with larger quantifies. Use of 10 ml each of hydrazine and nitrogen tetroxide simultaneously dumped into an open metal pan in a 140-cu ft laboratory hood produced an explosion, after several seconds of burning, which severly damaged the hood and split the seams of the metal pan. The overpressure acting on the hood was estimated to be at least 0.5 psi.

Further dumping tests were done outdoors. A total of 105 tests were made with various quantities of reactants up to 700 ml of combined fuel and oxidizer, and with various orders of dumping into open pans. In over 87 per cent of the tests, audible explosions resulted. Overpressures were measured ten feet away; in a series of tests in which 100 ml of fuel were dumped into 150 or 200 ml of oxidizer, overpressures ranging from 0.1 to 1 psi were recorded. In many tests, a sequence of two or three explosions occurred.

Other spill-test experiments have been reported by Rocketdyne (ref.6). In a test in which first 1.3 lb hydrazine and then 1.5 lb nitrogen tetroxide were spilled from a height of one foot on concrete, a series of explosions resulted with peak overpressures up to 2 psi at a station 10 feet way. A section of their report is quoted:

"The first of a series of overpressure shocks occurred anytime from immediately following ignition to several milliseconds later. Once started, shocks continued at periodic intervals until the main-flow control valves were closed. As before, film demonstrated that shock sources were in the product cloud at points several feet above the spill surface. Shock initiation was characterized by intense, white flashes as with the previous hydrazine fuel spill series. Once propellant flow had been terminated, surface burning of hydrazine continued to depletion, but evaporation of scattered droplets ceased and shock generation was no longer observed. There appeared

to be little question that the vapor-phase explosions were hydrazine-air reaction phenomena associated with fuel vaporization and admixture with air diffusion into the product cloud".

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The present authors cannot agree with the above interpretation of the explosions as vapor-phase hydrazine-air reaction phenomena. In the first place, liquid can easily be present several feet above the spill surface under the test conditions. In the second place, their model predicts explosions from hydrazine-air spill fires; while no such tests were made, smooth burning was reported for a test in which hydrazine was spilled on a painted wood surface previously saturated with nitrogen tetroxide. In the third place, our own tests (to be described below) show that explosions can occur under conditions in which air is excluded. In the fourth place, in a system where two oxidizers, nitrogen tetroxide and air, may be present, it is inherently unlikely that the explosion is caused by the less reactive oxidizer, air.

It may be advantageous to discuss, in a preliminary way, the reasonable alternate explanations of the explosion which frequently results when the fuel and oxidizer liquids are brought together, before the experimental results are presented.

One possibility to be considered is that the liquid fuel (either hydrazine or unsymmetrical dimethylhydrazine) can react as a monopropellant even in the absence of an oxidant, and  $\infty$  uld conceivably detonate if suitably triggered. However, Herickes, Damon, and Zabetakis (ref. 7) have shown that a 100-gram tetryl booster is unable to initiate detonation of either hydrazine or UDMH in a heavy steel tube under conditions where nitromethane explodes violently and ethylene oxide gives partial propagation. Hence, for the relatively unconfined geometry being considered, monopropellant detonation is ruled out.

In view of the known extreme rapidity of the energy release (a fraction of a millisecond), the required mixture of fuel and oxidizer must have become premixed prior to the explosion. Two reasonable possibilities exist:

- (1) liquid-liquid mixing, leading to exothermic formation of an explosive salt in solution;
- (2) vapor-vapor mixing, possibly leading to formation of an explosive aerosol salt.

No final choice between these alternatives is possible at the present. Also, it must be remembered that two distinct processes, initiation and propagation, may be involved. For example, initiation might occur by a gaseous process which provides energy to the liquid phase either to promote mixing, to ignite the already-mixed liquid, or both.

The liquid-liquid interface is extremely complex in itself because the exothermic mixing reaction must produce boiling, the resulting vapor tending to prevent further mixing if conditions are laminar, but perhaps promoting further mixing when and if a transition to turbulence occurs. Obviously, the

dynamics of the process become important, and particularly one needs to know if acceleration is occurring normal to an interface in the direction from the less-dense toward the more-dense fluid, leading to Taylor instability.

We have been

#### III. EXPERIMENTAL PROGRAM

#### A. GENERAL

From the background information reviewed above, it is clear that an explosion of some sort can occur when a hydrazine-type fuel liquid comes in contact with liquid nitrogen tetroxide under unconfined conditions. The precise mechanism is obscure. The lack of reproducibility in regard to occurrence, timing, and violence of the explosion in falling-droplet and dumping experiments strongly suggests that the fluid dynamics of the mixing process is critical.

In the present study, the approach has been to conduct experiments with only small quantities of the liquids (of the order of a few milliliters) under ideal laboratory conditions rather than field conditions. Apparatus of controlled geometry has been specially designed to permit initial liquid contact under conditions as reproducible as possible. The principal diagnostic tool has been high-speed photography with color film. In addition, special experiments of various sorts have been occasionally run in attempts to distinguish between alternate theories of the phenomenon.

The major effort has been centered around a geometry in which a thin barrier is suddenly removed from between the initially static liquids, leaving an orifice. One of the liquids may be slightly pressurized so that it will flow through the orifice into the other liquid, the resulting events being observed. Orifice size and pressure differential are controllable variables.

As a preliminary to this study, falling-droplet experiments were undertaken while the more complex apparatus for the interface experiments was being designed and constructed.

The implicit assumption in this work is that rather complete understanding of small-scale phenomena is a necessary prerequisite for rational scaling procedures and evolution of suppression techniques.

#### B. FALLING-DROPLET EXPERIMENTS

#### 1. Objectives

When a droplet falls into a liquid pool, a very complex dynamic process of crater formation and droplet break-up occurs. Photographs have been published (ref. 8). This process being so complex even with chemically inert liquids, there is little hope that a thorough dynamic analysis of a reactive hydrazine droplet falling into a nitrogen tetroxide pool can be made. Nonetheless, there is the possibility that useful empirical information

can be obtained from careful droplet experiments, particularly with regard to probability of explosion versus droplet height. It also may be informative to vary the temperature and hence the vapor pressure of the nitrogen tetroxide, or to perform the experiment in an inert rather than an air atmosphere. The tests have been performed with these objectives in mind.

#### 2. Experimental Procedure

The principal variables are drop size and impact velocity. The reproducibility of drop size obtainable in a steady-state sequence of drops from a standard burette was determined by weighing a sequence of water drops, of about 0.04-gram average size. The variation was found to be approximately ± 10 per cent.

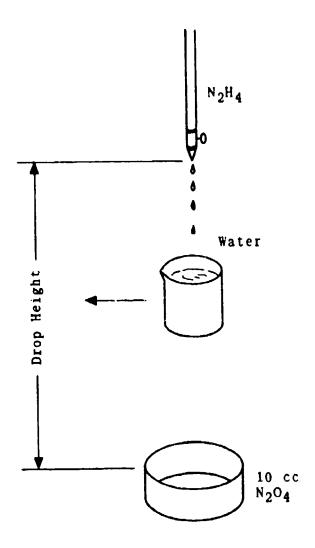
The initial experiments consisted of a study of the reproducibility of the explosion as a function of drop height. The experiments were carried out in a vent hood, which limited the maximum drop height to 25 inches. A schematic diagrem of the apparatus is shown in Figure 1. A standard burette was mounted over an aluminum dish, with a shallow pan of water on a swivel support interposed between. The separate reactants were put in the burette and dish respectively, a steady drop rate established, and the intermediate pan of water then removed from the drop path by pulling a cord. The temperature of the nitrogen tetroxide at this time would be about 10°C. A sharp report was taken to be the indication of explosion. If the first drop impacting on the other hypergolic liquid did not lead to explosion, subsequent drops were allowed to fall at a steady rate of one every two or three seconds until an explosion occurred or the reactant in the dish became depleted. Modifications of this procedure were made for special tests, as described in the next section.

#### 3. Results

No explosions were obtained in two experiments each at heights of 11, 17, and 25 inches, when nitrogen tetroxide was dropped into hydrazine. When hydrazine was dropped into nitrogen tetroxide, frequent explosions resulted, so a body of data was obtained with this arrangement. Results are summarized in Figure 2, in which each point plotted represents a group of at least 20 drops, except for the smallest drop height tested, 1.5 inches. In this case no explosions were obtained in 10 trials. For greater heights, the probability of explosion is seen to increase with increasing height. At the greatest height tested, 25.2 inches, the probability of explosion was 80 per cent. Data for the first drop of a sequence and for all drops are seen to compare fairly well with one another.

The data suggest that critical mixing conditions are required to initiate the explosion, and that the probability of obtaining these critical conditions increases with increasing energy of impact.

Further experiments with talling drops of hydrazine were conducted to determine if the parameters of nitrogen tetroxide temperature and ambient atmosphere composition would have any significant effect on the explosion



Drop Size - 1/27 cc Drop Rate - 20 to 30 Drops/Min.

Figure 1. Schematic Diagram-Falling Droplet Apparatus.

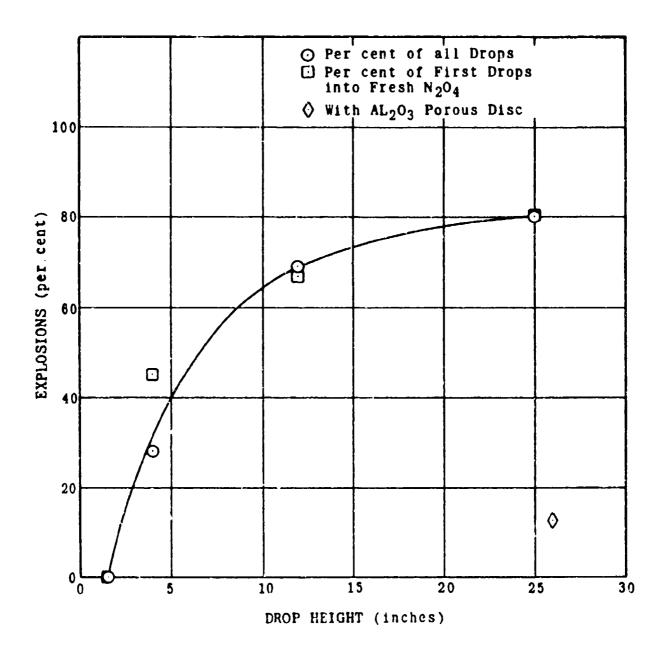


Figure 2. Explosion Probability Versus Drop Height-Falling Droplet Apparatus.

phenomenon. The dimensional parameters of the experiments were held constant at a 26-inch drop height and drop size approximately 1/27 milliliter, with the following results:

Exp	eriment Description	Total No.	No. of Explosions	Per Cent Explosions
1.	N <sub>2</sub> O <sub>4</sub> allowed one minute residence in aluminum weighing	23	14	71
	dish surrounded by ice-water bath			
2.	Broad jet of N <sub>2</sub> across surface of	45	24	53
	N <sub>2</sub> O <sub>4</sub> at room temperature			
3.	3.5-inch-high sleeve around	28	22	78
	N <sub>2</sub> O <sub>4</sub> dish, purged with N <sub>2</sub>			
4.	3.5-inch-high sleeve around	47	25	53
	N2O4 dish, purged with air			

In addition, it was found from three experiments that an explosion could occur when the second drop of hydrazine (of a sequence at two drops) contacted <u>frozen</u> nitrogen tetroxide.

The foregoing experiments suggest that neither the initial presence of air nor the initial temperature and vapor pressure of nitrogen tetroxide have measurable influence on probability of explosion.

Another set of droplet tests was made with the hydrazine droplets impinging on a porous aluminum oxide block (pore size 1/4 mm) with the nitrogen tetroxide liquid level about one millimeter below the upper surface of the block. This geometry greatly reduced but did not eliminate the probability of explosion. The probability data are plotted in Figure 2. This result, while not constituting proof, is consistent with the view that liquid-liquid mixing (prevented by the porous block) is a necessary prerequisite to the explosion.

#### C. LIQUID-LIQUID INTERPACE EXPERIMENTS

#### 1. Objectives

The purpose of these experiments has been: to bring the fuel and oxidizer liquids together under strictly controlled conditions, involving withdrawal of a Teflon separator; to vary pressure differential as required to produce reproducible explosions; and to determine the nature of these explosions by high-speed photography and theoretical calculations.

#### 2. Apparatus

A small apparatus to permit rapid contact between the surfaces of the two liquids while minimizing initial flow disturbances was designed and

constructed. A schematic diamgram of this apparatus is shown in Figure 3, and a photograph of the complete laboratory set-up appears as Figure 4.

In operation, the piston is cocked and latched, the lower glass cell positioned and covered with a small sheet of Teflon clamped in the piston, and the upper cell positioned and held in contact with the Teflon sheet by four small spring plungers. The assembly is then clamped on a support bar in the fume hood, the latch linked to a triggering solenoid, and the assembly cooled by application of dry ice to reduce fuming of the nitrogen tetroxide. Nitrogen tetroxide is introduced into the botton of the lower cell by dropper through the tubing extension at the side, a small notch (approximately 0.060" wide by 0.020" deep) in the upper surface of the lower cell permitting escape of most of the vapor which is formed. The fume hood is then closed, and hydrazine introduced into the upper cell from a squeeze bottle outside the hood through 1/8-inch polyethylene tubing. Triggering is then accomplished by manual switching of the solenoid, or by a switch in the high-speed camera control box when motion pictures are desired.

The upper surface of the lower glass cell and the lower surface of the upper glass cell are polished to facilitate the motion of the Teflon sheet. Cells, both circular and square in cross section, were fabricated; the circular cells (0.5-inch ID) for initial trials, and the square-section cells  $(0.5\text{-inch}\times 0.5\text{-inch}$  internal) to allow undistorted photography of events at the interface.

A variety of Teflon sheet configurations were used, and three modifications of the method of introducing fluid into the lower cell were made. The purpose of these modifications was to permit the application of moderate pressures to the fluid in the lower cell in order to produce a jet when the Tefi sheet is moved so as to position a perforation in the sheet between the un and lower cells. The first modification consisted of an auxiliary champe, with a flexible Teflon bellows loaded by weights and the necessary valving to load the chamber. This auxiliary chamber provided no useful experimental results because of difficulty in obtaining a sufficiently flexible bellows. For experiments at moderate jet velocities, this auxiliary chamber was replaced by a stainless steel thistle tube (0.180-inch ID) which permits application of a static head of up to 12 inches on the liquid in the lower cell. Purging of the lower cell at these low pressures is readily accomplished by manually lifting the upper cell, and an adequate seal is provided by the spring-plunger loading of the upper cell. For experiments at lower cell internal pressures of up to 30 inches of mercury above atmospheric pressure, the auxiliary chamber was modified to allow nitrogen pressurization, and a hypodermic bleed line added, with its openings a few thousandths of an inch below the top of the lower cell.

#### Static-Interface Experiments

Two initial trials were made with the static-interface apparatus without high-speed photography. Unexpectedly, both resulted in rather violent explosions. In each case approximately I milliliter of hydrazine was used in the upper cell. There was no orifice in the Teflon separator, the plan being to pull it completely from the region between the cells. A third run, an

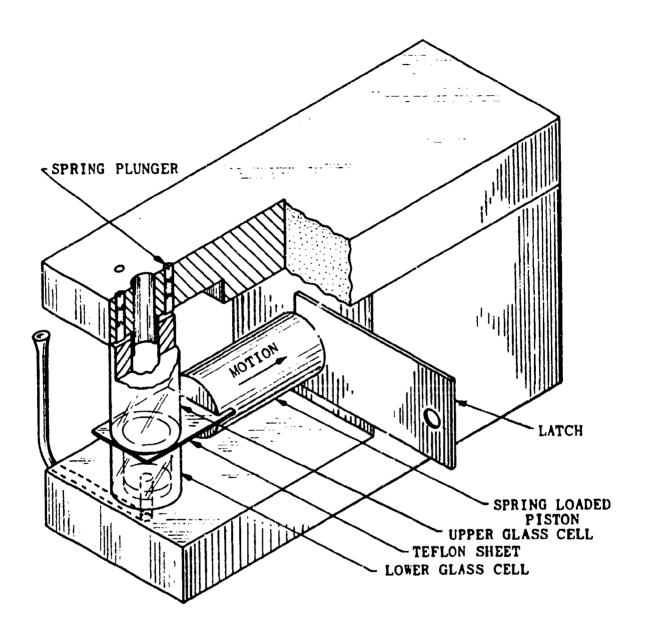


Figure 3. Schematic Diagram of Apparatus
For Generation of
Liquid-Liquid Interface.

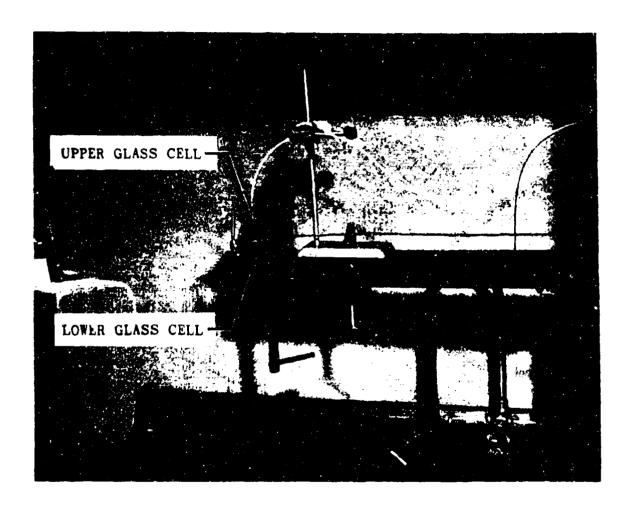


Figure 4. Arrangement for Production and Observation of Liquid-Liquid Interface.

attempt to obtain a 7000 frames/sec motion picture close-up, resulted in a somewhat less violent explosion, which occurred between frames well before the camera had completed acceleration (framing rate about 3000/sec). The fourth experiment resulted in an explosion comparable in violence to the third, and the significant portion of the film record is shown in Figure 5 (framing rate 6890/sec). While the origin of explosion is not evident from this figure, we postulated that the impact of the spring-loaded upper glass cell on the lower cell when the separator was withdrawn was responsible for the explosion.

An additional series of experiments (Table I, Runs 1-6) was therefore conducted to determine if elimination of any impact of the cells would reduce the probability of an explosion. (These were the first numbered runs). Five runs were made in which an extended 0.003-inch-thick Teflon sheet was used with a "U" shaped portion, approximately 1/2-inch wide, cut out of the end of the sheet. This arrangement was intended to prevent the upper cell from moving when the liquids were brought into contact. In four or these runs, no explosion occurred, and the extended portion of the Teflon sheet remained between the cells. In one run, a portion of the Teflon sheet wrinkled or tore, and an explosion was produced. An additional run designed to provoke an explosion by complete removal of a 0.020-inch-thick sheet did successfully produce an explosion. Twelve more experiments (Table I, Runs 8-19) with 0.003-inch-thick sheets perforated by single orifices ranging from 0.125-inch to 0.344-inch in diameter produced no explosions. In all the above experiments, nitrogen tetroxide was used in the lower cell with the liquid level in the filling tube being little, if any, distance above the level of the interface between the upper and lower cells. Approximately 1 milliliter of hydrazine (the less dense fluid) was used in the upper cell.

High-speed motion pictures at approximately 7000 frames/second were taken of one of the experiments with the "U" shaped cutout sheet. The initial contact of the reactants appears to produce a violent vapor evolution which throws most of the hydrazine from the upper cell.

From these static-interface tests, it may be concluded that the initial liquid-liquid mixing is not adequate to produce an explosion in the absence of impact of the cells. This was the expected result; however, the vapor evolution which rather promptly throws the upper liquid out of its cell had to be kept in mind in planning the later experiments. This situation implies that if the explosion does not occur rather promptly after contact, the ejection of the upper liquid effectively terminates the test. The available test time presumably can be somewhat prolonged by using smaller orifices in the separator.

#### 4. Jet-Injection Experiments

The initial attempts to use the weighted-bellows auxiliary pressure chamber previously described were not successful because of difficulties in purging and then adequately sealing the lower cell at pressures of a few psi, as well as excessive stiffness of the bellows. The pressures which may be obtained by keeping the free surface of the liquid in the lower cell up to

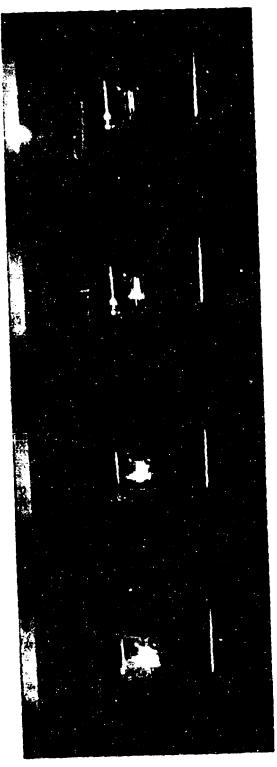


Figure 5. High-Speed Motion Picture Sequence of N<sub>2</sub>H<sub>4</sub>-N<sub>2</sub>O<sub>4</sub> Explosion 6890 Frames Per Second (Static Interface).

TABLE I

LOG OF INTERFACE EXPERIMENTS WITH AND WITHOUT INJECTION

Remarks	Fire Only	Fire Only	Fire Only	Exploded. Probably wrinkling of Teflon sheet.	Fire only. Motion picture @ 7000 frames/sec.	Exploded. Motion picture @ 7500 frames/sec. Teflon sheet completely removed, upper cell tilted and explosion appeared to initiate in area of glass contact.	Exploded
Cell Type	Circular	Circular	Circular	Circular	Square	Square	Square
Pressure in Lower Cell	0	0	0	0	0	•	O
Teflon Sheet Configuration	0.003" Thick U Shape	0.003" Thick U Shape	0.003" Thick U Shape	0.003" Thick U Shape	0.003" Thick U Shape	0.020" Thick	0.020" Thick Oval Cutout
Fluid in Upper Cell	N2H4 1 cc	N <sub>2</sub> H <sub>4</sub> 1 cc	N <sub>2</sub> H <sub>4</sub> 1 cc	N <sub>2</sub> H <sub>4</sub> 1 cc	N <sub>2</sub> H <sub>4</sub> 1 cc	N <sub>2</sub> H <sub>4</sub> 1 cc	N2H4 1 cc
Fluid in Lower Cell	N204 8.9°C	N <sub>2</sub> 0 <sub>4</sub> 8°C	N <sub>2</sub> 0 <sub>4</sub> 8.5°C	N204 13°C	N <sub>2</sub> 04	N <sub>2</sub> O <sub>4</sub>	N204
Run No.	-	2	m	4	so	9	7

Annual Principal Principal

TABLE I (Cont'd.)

Remarks	Fire Only	Fire Only	Fire Only	Fire Only	Fire Only	Fire Only	Fire Only	Fire Only	Fire Only	Fire, slight pop after approximately 1 rec.
Cell Type	Circular	Círcular	Circular	Circular	Circular	Circular	Circular	Circular	Circular	Circular
Pressure in Lower Cell	0	0	0	0	0	0	0	0	0	0
Teflon Sheet Configuration	0.003" Thick 3/16" dia. hole	0.003" Thick 3/16" dia. hole	0.003" Thick 3/16" dia. hole	0.003" Thick 5/32" dim. hole	0.003" Thick 5/32" dia. hole	0.003" Thick 5/32" dia. hole	0.003" Thick 11/32" dia. hole	0.003" Thick 11/32" dia. hole	0,003" Thick 11/32" dia. hole	0.003" Thick 11/32" dia. hole
Flufd in Upper Cell	N2H4 1 cc	N2H4 1 cc	N <sub>2</sub> H <sub>4</sub> 1 cc	N <sub>2</sub> H <sub>4</sub> 1 cc	N2H4 1 cc	N <sub>2</sub> H <sub>4</sub> 1 cc	N <sub>2</sub> H <sub>4</sub> 1 cc	N2H4 1 cc	$^{N_2H_4}_{2}$	N2H4 1 cc
Fluid in Lower Cell	N204	N204	N <sub>2</sub> 0 <sub>4</sub>	N <sub>2</sub> O <sub>4</sub>	7 <sub>G</sub> <sup>Z</sup> N	N <sub>2</sub> O <sub>4</sub>	N204	N <sub>2</sub> O <sub>4</sub>	N204	N204
Run No.	ω	σ	10	11	12	13	14	15	16	17

TABLE I (Cont'd.)

Remarks	Pire Only	Fire Only	Fire only. Color motion picture @ 2040 frames/sec.	Exploded, Color motion picture @ 2040 frames/sec.	Exploded	Fire Only	Fire, 2 slight pope	Burned approximately 1.5 seconds, then exploded.	Fire Only	Fire Only
Cell Type	Circular	Circular	Square	Square	Circular	Circular	Circular	Circular	Cfrcular	Circular
Pressure in Lower Cell	0	0	12" Head $(N_2O_4)$	12" Head $(N_2H_4)$	0	12" Head $(N_2^0_4)$	12" Head	12" Read	12" Head	12" Head
Teflon Sheet Configuration	0.003" Thick 11/32" dia. hole	0.003" Thick 11/32" dia. hole	0.003" Thick 1/8" dia. hole	0.003" Thick 1/8" dia. hole	0.003" Thick 1/8" dia. hole	0.003" Thick 1/8" dia. hole	0.003" Thick 1/8" dia. hole	0.003" Thick 1/8" dia. hole	0.003" Thick 0.045" dia. hole	0.003" Thick 0.045" dia. hole
Fluid in Upper Cell	N <sub>2</sub> H <sub>4</sub> 1 cc	N2H4 1 cc	N2H4 1 cc	$N_2O_4$ $\sim 2 \text{ cc}$	N <sub>2</sub> 04 ~ 2 cc	N2H4 1 cc	N2H4 3 cc	N2H4 3 cc	N2H4 3 cc	N2H4 3 cc
Fluid in Lower Cell	N <sub>2</sub> 0 <sub>4</sub>	N <sub>2</sub> 0 <sub>4</sub>	N <sub>2</sub> O <sub>4</sub>	$^{N_2H_4}$	7H <sup>Z</sup> N	N204	N204	N2 V	N204	N204
Run No.	18	19	20	21	22	23	54	25	56	27

TABLE I (Cont'd.)

Remarks	Fire Only	Fire Only	Exploded	Fire Only	Fire Only	Fire Only	Fire Only	Fire Only	Fire only. Color motion picture @ 2500 frames/sec
Cell Type	Circular	Circular	Circular	Circular	Circular	Circular	Circular	Circular	Square
Pressure in Lower Cell	12" Head	12" Head	2" Head	2" Head	6" Head	6" Head	6" Head	6" Read	0
Teflon Sheet Configuration	0.003" Thick 0.020" dia. hole	0.003" Thick Triangular per- foration. Length of each side approx. 0.040"	0.003" Thick 0.020" dia. hole	0.003" Thick 0.020" dia. hole	0.003" Thick 0.020" dia. hole	0.003" Thick 4 holes 0.020" dia. spaced on 1/16" radius	0.003" Thick 0.012" dia. hole	0.003" Thick 0.36" dia. hole	0,003" Thick 1/8" dia. hole
Pluid in Upper Cell	N2H4 3 cc	N <sub>2</sub> H <sub>4</sub> 3 cc	N2H4 3 cc	N <sub>2</sub> H <sub>4</sub> 3 cc	N <sub>2</sub> H <sub>4</sub> 3 cc	N2H4 3 cc	N <sub>2</sub> H <sub>4</sub> 3 cc	N2 <sup>H</sup> 4.	N <sub>2</sub> 0 <sub>4</sub> 2 cc
Fluid in Lower Cell	N204	N204	N <sub>2</sub> O <sub>4</sub>	N <sub>2</sub> 0 <sub>4</sub>	N204	N 204	N <sub>2</sub> O <sub>4</sub>	N204	7 <sub>H</sub> <sup>2</sup> N
Run Ko.	28	53	30	31	32	33	35	35	36

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Remarks	Two small explosions.	Light Explosion	Exploded. Color motion picture @ 2500 frames/sec.	Light Explosion	Fire Only. Color motion picture @ 1400 frames/sec.	Exploded. Color motion picture @1600 frames/sec.	Exploded. Color motion picture @ 2600 frames/sec.	Fire Only. Color motion picture @ 2600 frames/sec.	Fire Only, Color motion picture @ 2600 frames/sec.
Cell Type	Square	Square	Square	Square	Square	Square	Square	Square	Square
Pressure in Lower Cell	12" Head	12" Head	12" Head	11" Hg	9" 78	28.5" Hg	25.5" Нв	18" нв	24" Hg
Teflon Sheet Configuration	0.003" Thick 1/8" dia. hole	0.003" Thick 1/8" dia. hole	0.003" Thick 1/8" dia. hole	0.020" Thick 1/8" dia. hole	0.020" Thick 0.020" dia. hole	0.020" Thick 0.020" dia. hole	0.020" Thick 0.020" dia. hole	0.02C" Thick 0.02C" dia. hole	0.020" Thick 0.020" dia. hole
Pluíd in Upper Cell	N <sub>2</sub> 0 <sub>4</sub> 2 cc	N <sub>2</sub> 04 2 cc	N <sub>2</sub> 04 4 cc	N <sub>2</sub> H <sub>4</sub> 3 cc	N <sub>2</sub> H <sub>4</sub>	N <sub>2</sub> H <sub>4</sub>	N2H4 4 cc	N2H4 4 cc	N <sub>2</sub> H <sub>4</sub> 4 cc
Fluid in Lower Cell	N2H4	N2H4	7,H <sup>2</sup> N	70 <sup>2</sup> N	7 <sub>2</sub> 2 <sub>N</sub>	N <sub>2</sub> 0 <sub>4</sub>	N2 <sup>0</sup> 4	N2 <sup>0</sup> 4	N204
No.	37	38	39	07	17	77	43	77	45

TABLE I (Cont'd.)

Remarks	Fire Only. Color motion picture @ 3000 frames/sec.	Fire Only. Color motion picture @ 6500 frames/sec.	Fire Only. Color motion picture @ 6500 frames/sec.	Fire Only. Color motion picture @ 6500 frames/sec.
Cell Type	Square	Square	Square	Square
Pressure in Lower Cell	28" нв	28" нѕ	26" H8	28" нв
Teflon Sheet Configuration	0.020" Thick 0.020" dia. hole	6.020" Thick 0.020" dia. hole	0.020" Thick 0.020" dia. hole	0.020" Thick 0.020" dia. hole
Fluid in Upper Cell	N <sub>2</sub> H <sub>4</sub> 4 cc	N <sub>2</sub> H <sub>4</sub> 4 cc	N <sub>2</sub> H <sub>4</sub> 4 cc	N <sub>2</sub> H <sub>4</sub> 4 cc
Flufd in Lower Cell	N204	N204	N204	N204
Run No.	97	47	84	67

12 inches above the cell interface presented no difficulties, however, and a series of 20 experiments (Table I, Runs 20-39) were carried out with this configuration, with various orifice sizes. A head of 12 inches of nitrogen tetroxide is calculated to produce a jet velocity at the orifice of 240 cm/sec, neglecting friction, after an initial acceleratory period to be discussed later.

To achieve higher injection velocities, the nitrogen pressurization technique was used, with nitrogen pressures up to 28.5 inches Hg. This corresponds to a steady-state jet velocity of 1160 cm/sec, after acceleration and neglecting friction. Ten experiments (Table I, Runs 40-49) were carried out with nitrogen pressurization of the lower liquid.

In all the above tests except Runs 21, 22, 36, 37, 38 and 39, the lighter liquid, hydrazine, was placed in the upper cell and the heavier liquid, nitrogen tetroxide, in the lower cell. The six runs with hydrazine in the lower cell will be discussed later.

Of the 24 runs with injection of nitrogen tetroxide into hydrazine, explosions occurred in three of the ten runs at high injection rates and two of the fourteen runs at low injection rates. Thus no reproducible explosion could be achieved by this technique within the range of velocities explored. Nevertheless, some interesting results were obtained which are discussed here.

Figures 6, 7, and 8 show results from selected runs (42, 43, 20). Whether or not explosion occurs, an interface is always seen rising from the orifice a few milliseconds after the perforated separator has been pulled into place. This interface must be a gas bubble generated by the reaction between the two liquids. When explosion occurs, it occurs some time after bubble appearance, during which violent mixing and reaction are taking place. In Runs 42 and 43, 10.0 and 11.5 milliseconds, respectively, elapsed from first bubble appearance to explosion. In these same runs, pronounced brightness (characterized by milky-white appearance on the color films) appeared 5 and 4.2 milliseconds before explosion respectively.

The volumetric growth rate of the bubble seen in the first few frames was calculated for 6 runs, including two explosions, with the assumption that the bubbles are rotationally symmetrical about a vertical axis. These volumetric growth rates, plotted in Figure 9, show a run-to-run variation which does not correlate with nitrogen tetroxide pressure, nor are there any significant features of these curves which would indicate an incipient explosion. The identity of the observed front as a gas bubble rather than a liquid-liquid interface is established by calculation of the maximum possible flow rate of the liquid through the orifice at the existing pressure differential. For example, in Run 42, the steady-state liquid velocity of 1160 cm/sec with an orifice area of 0.0020 sq cm yields a volumetric liquid rate of 0.0023 ml/millisec., while bubble growth rate from Figure 9 is 114 times as great.

It is instructive to calculate the gas volume produced by boiling nitrogen tetroxide liquid at  $21^{\circ}$ C to give the equilibrium  $NO_2:N_2O_4$  gas mixture at one atmosphere (mean molecular weight = 79). On this basis one obtains 438 volumes of gas per volume of liquid. If, instead of simple vaporization,

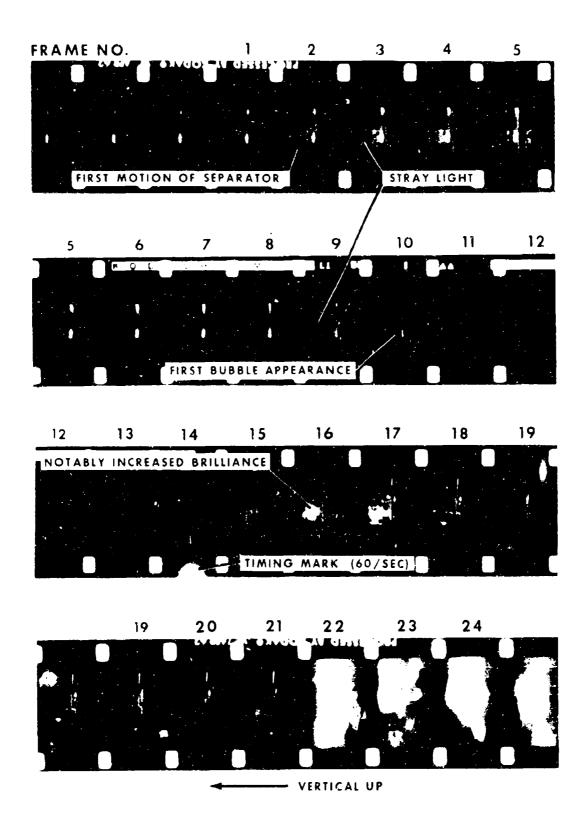


Figure 6. Explosion (Run 42) Photographed at 1600 Frames/sec. Nitrogen Tetroxide under 28.5-Inch-Hg Pressure Injected Upward through 0.020-Inch Orifice into Hydrazine (4 ml).

#### FIRST MOTION OF SEPARATOR OCCURS IN FRAME NO. I

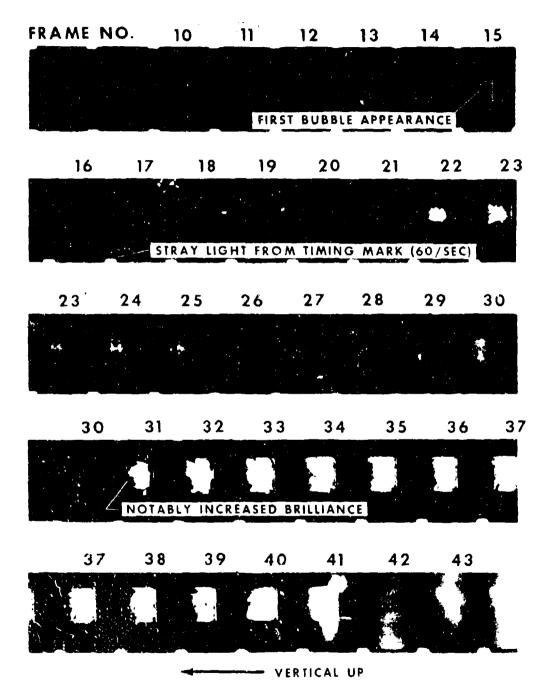


Figure 7. Explosion (Run 43) Photographed at 2600 Frames/sec. Nitrogen Tetroxide under 25.5-Inch-Hg Pressure Injected Upward through 0.020-Inch Orifice into Hydrazine (4 ml).

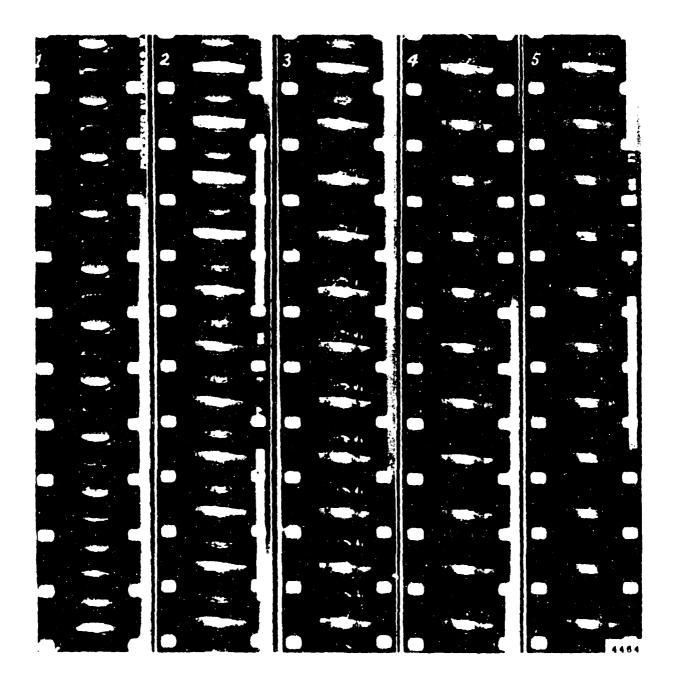


Figure 8. Non-Explosive Reaction (Run 20) Photographed at 2040 Frames/sec. Nitrogen Tetroxide under 12-Inch Head Injected Upward through 0.125-Inch Orifice into Hydrazine (1 ml).

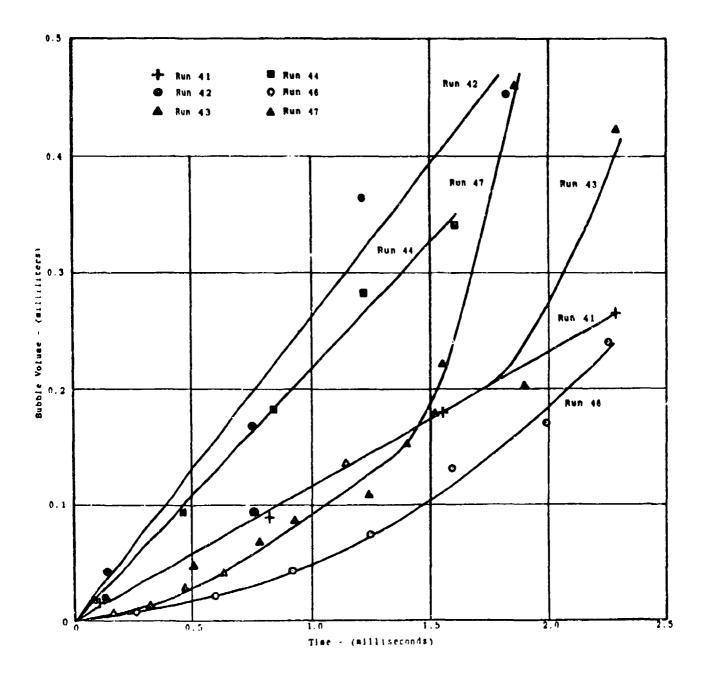


Figure 9. Bubble Volume Versus Time for Six Jet-Injection Experiments.

one assumes adiabatic chemical reaction to products at 2990°C:

$$N_2O_4(1iq) + 2N_2H_4(1iq) \longrightarrow 3N_2 + 4H_2O (gas)$$

one obtains 29200 volumes of gas per volume of liquid nitroken tetroxide.

Since the measured bubble growth rate (Figure 9) is only of the order of 100 times the liquid flow rate, it is possible to account for the bubble by assuming that roughly 1/4 of the entering liquid vaporizes to produce cold nitrogen tetroxide vapor, the heat of vaporization being supplied by rapid chemical reaction at the interface.

Some consideration must also be given to the transient aspect of the orifice flow; i.e., a finite time must be required for the flow rate to accelerate to the steady-state value specified by the orifice flow equation. In cases such as Run 42, where the orifice diameter is very small relative to the lower cell and connecting tubing, and the pressure is 28.5 inches Hg, the transient time is calculated to be about 0.2 milliseconds. (This calculation assumes that a cylinder of liquid of diameter d (orifice diameter) and length 2d must accelerate under the acting pressure to the terminal velocity, in accordance with Newton's Second Law.)

In cases such as Run 20, where the orifice diameter (0.125-inch) is comparable with the supply tube diameter (0.180-inch) and the head is only 12 inches of nitrogen tetroxide acted on by gravity rather than nitrogen pressure, the acceleration is much slower, since the entire column of liquid in the thistle tube can accelerate no faster than one g. The area ratio of thistle tube to orifice being 2.08, the acceleration at the orifice can be no more than 2.08 g, or 2040 cm/sec<sup>2</sup>. At this rate, over 100 milliseconds is required to reach terminal velocity. Frame-by-frame analysis of Figure 8 (Run 20) shows that about 8 milliseconds elapsed between first liquid-liquid contact and an observable bubble. During this time the liquid flowing through the orifice could have moved only a distance of at 2/2 or 0.065 cm.

This is further confirmation of the view that a gas-forming reaction initiates at the interface before much liquid injection has occurred. In Run 20, the gas displaced the hydrazine from the upper cell in a few milliseconds. In Runs 42 and 43, violent reaction in the gas-liquid region, presumably with turbulence and generation of new interface, took place in the interval before explosion occurred. However Table I shows a number of runs similar to 42 and 43 except that there was no explosion, so clearly the pertinent parameters were not adequately controlled.

Six runs ("able I, Runs 21 and 22, 36 to 39) were made with hydrazine, the lighter liquid, in the lower cell and free surface elevations of 0 to 12 inches. Three resulted in violent explosions, two in minor explosions, and one (at zero head), no explosion. A high-speed motion picture, in color at 2040 frames per second, was obtained for the case with the 12-inch hydrazine surface elevation. A portion of this film strip is reproduced here as Figure 10. The explosion can be seen in the 51st frame of the figure. The portion of this strip prior to that shown reveals a delay of 92 milliseconds after which a jet, apparently of liquid hydrazine, is seen in the upper cell. Much of the

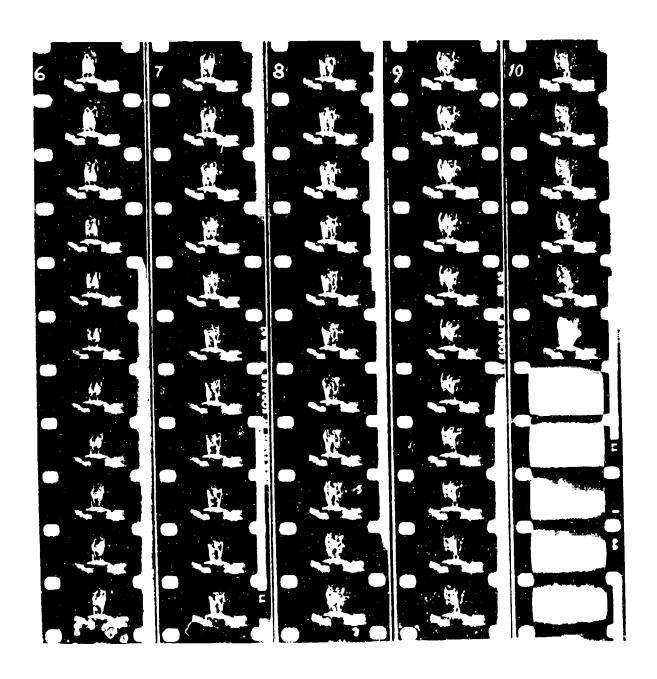


Figure 10. Explosion (Run 21) Photographed at 2040 Frames/sec. Hydrazine under 12-Inch Head Injected Upward through 0.125-Inch Orifice into Nitrogen Tetroxide.

nitrogen tetroxide liquid has been ejected upward from the upper cell in the interval prior to the appearance of this jet. We interpret this film by assuming that some of the denser nitrogen tetroxide from the upper cell had somehow gotten into the lower cell shortly after the slide had been moved into place. Burning and vapor evolution is assumed to have initiated below the slide and created a pressure which accelerated the nitrogen tetroxide but delayed formation of the hydratine jet. No definite statement is possible about the origin of the explosion.

#### D. GAS-LIQUID EXPERIMENTS

#### 1. Objectives

One possible origin of the explosion is formation of a dissolved explosive reaction product with either the liquid fuel or liquid oxidizer as solvent. Experiments to produce such an explosive substance were attempted. Simultaneously it is informative to observe the interaction of nitrogen tetroxide vapor (diluted with nitrogen) with liquid hydrazine.

#### 2. Apparatus

A small flow of nitrogen was bubbled through liquid nitrogen tetroxide maintained at ice temperature (one or two bubbles/sec). The effluent gas was passed through a glass tube terminating in a capillary tip which was immersed in liquid hydrazine either at room temperature or ice temperature. In the course of experimentation, variations of flow rate were made as well as reversal of position of hydrazine and nitrogen tetroxide in the apparatus.

#### 3. Results

In no case did explosions occur, even when the experiment was continued until the second liquid was evaporated to dryness.

When the nitrogen stream (saturated with nitrogen tetroxide vapor at 0°C) flowed into the liquid hydrazine at a slow rate, the bubbles leaving the hydrazine contained a white smoke. This is presumably the same substance reported by others (refs. 2,5) to form when the two vapors in diluted form are brought into contact, and may consist at least in part of ammonium nitrate. The hydrazine liquid gradually darkened to a reddish color as the experiment proceeded. When the last of the hydrazine evaporated, a tiny trace of residue was observed but not analyzed. If the foregoing procedure was varied by increasing the nitrogen flow rate, occasional flashes of orange flame would seen at the tip of the capillary. Each flash only persisted for a fraction of a second, and was presumably associated with a single bubble. Only occasional bubbles would ignite, so the phenomenon was quite sporadic. On raising the nitrogen tetroxide temperature and further increasing the nitrogen flow rate, a condition could be reached in which a fairly steady flame cone would maintain itself on the submerged capillary tip.

When the liquids were reversed, the passage of the hydrazine-containing nitrogen through nitrogen tetroxide gave no observable flame or other

spectacular event until evaporation to dryness. The hydrazine (at room temperature) has of course a much lower vapor pressure than nitrogen tetroxide.

#### IV. PRESENT STATUS OF KNOWLEDGE AND RECOMMENDED FUTURE WORK

The positive results of this one-year study are listed:

- 1. The probability of explosion when a hydrazine droplet fell into a pool of nitrogen tetroxide increased gradually with increasing distance of free fall, seven inches corresponding to 50 per cent probability.
- 2. Impact of one spring-loaded glass cell on another when a separator is removed in the presence of hydrazine and nitrogen tetroxide (liquids and/or vapors) reproducibly gave explosion (five times in five tests).
- 3. Injection of a jet of liquid nitrogen tetroxide into liquid hydrazine through a 0.020-inch orifice under a pressure ranging from 19 to 28.5 inches Hg with no solid-solid impact led to explosion twice in eight tests. Each of the two explosions occurred about 10 milliseconds after the first appearance of a bubble, with apparently violent mixing and reaction in the interim.
- 4. When a liquid-liquid interface was formed without injection and without solid-solid impact, no explosion occurred in 16 tests with the lighter liquid in the upper cell.

The lack of reproducibility in the droplet and particularly the injection tests prevented any precise determination of effects of the controllable parameters on the critical conditions for explosion. Also, the lack of reproducibility interfered with development of really good photographic techniques for studying the phenomenon. At this time, therefore, no conclusive picture of the explosion mechanism can be presented. The two most likely mechanisms are, in our opinion:

- A. The two liquids on contact produce vapors rich in nitrogen tetroxide (the more volstile) but also containing an aerosol which is a still-explosive reaction product or adduct of the fuel and oxidizer. If turbulent mixing (generated by initial relative velocity and subsequent shear, by gas evolution, by localized heat liberation, or by interfacial instability) is able to promote formation of a sufficient concentration of this aerosol adduct, an explosion occurs. Or:
- B. When the two liquids come into contact, vapor generation tends to separate them again but if turbulent mixing is adequate, a sufficient quantity of one liquid (probably nitrogen tetroxide) is able to dissolve in the other liquid to form a soluble explosive adduct which explodes if a sufficiently high concentration level is reached in a region of adequate size.

The evidence discussed in Section III of this report is inadequate for choice between these mechanisms. It is also possible that neither of these mechanisms is correct. However all the observations are believed to be consistent with either of these explanations and quite inconsistent with others such as a monopropellant detonation or a hydrazine vapor-air explosion.

If one accepts the idea that the precise nature of the three-phase turbulent mixing of the two fluids is critical to the formation of an explosive substance, one needs far more detailed information on the critical mixing requirement than is available in order to predict scaling effects or suggest practical means for reducing the probability of explosion.

The problem remains and calls for solution. It is reminiscent of the "knock" reaction in internal combustion engines, the mechanism of which has been studied without final resolution for many years (although means for control have been found). As long as hydrazine-type liquids and nitrogen tetroxide are to be used on a large scale as storable liquid rocket fuels, the problem is important. Indeed, other chemical systems of storable liquids, such as pentaborane-chlorine trifluoride, would be expected to exhibit similar behavior.

If further research effort to study the explosive reactions of unconfined hypergolic liquids is undertaken, the present authors suggest that the effort be planned to permit tests over several years, with the utmost attention to geometric characteristics of the test procedures. A variety of test procedures should be explored. The liquid configuration used in this study should be further explored at even higher injection velocities. The possible effects of initial nitrogen tetroxide temperature and prior vapor bubbles in the nitrogen tetroxide on probability of explosion should be examined. The reproducibility of injection velocity and state of turbulence when one inert liquid is injected into another should be studied. Attention should be given to the initial 0.003-inch air bubble in the separator orifice; by modifying the apparatus, the orifice could contain one of the two liquids.

Other geometries which might be worth exploring include the use of separate jets of each liquid at controlled velocities which are allowed to intersect. This experiment however appears to require larger quantities of the dangerous materials than the separator geometry employed by us.

Experiments in which nitrogen tetroxide vapor <u>not</u> diluted with nitrogen is allowed to flow at various velocities from a nozzle and impinge on liquid hydrazine might be informative.

A strictly gas-phase experiment is conceivable in which the two vapors are separated by a singly or multiply perforated barrier sealed by thin foil which is ruptured by a pressure differential. The resulting rapid gaseous mixing would of course lead to violent combustion. The nature of the resulting rapid pressure rise could then be studied in detail.

Chemical experiments to determine the nature of the smoke produced when dilute nitrogen tetroxide vapor is passed through liquid hydrazine might be helpful, as well as analysis of the residual liquid.

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Occasional explosions occurred, preceded by bubble formation. Alternate theories of the photography, gave non-reproductble results. explosion phenomenon are discussed.

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